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Fate and bioavailability of arsenic in organo-arsenical pesticide-applied soils. Part-I: incubation study

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Abstract

A laboratory incubation study was conducted to estimate geochemical speciation and in vitro bioavailability of arsenic as a function of soil properties. Two chemically-variant soil types were chosen, based on their potential differences with respect to arsenic reactivity: an acid sand with minimal arsenic retention capacity and a sandy loam with relatively high concentration of amorphous Fe/Al-oxides, considered a sink for arsenic. The soils were amended with dimethylarsenic acid (DMA) at three rates: 45, 225, and 450 mg/kg. A sequential extraction scheme was employed to identify the geochemical forms of arsenic in soils, which were correlated with the "in vitro" bioavailable fractions of arsenic to identify the most bioavailable species. Arsenic bioavailability and speciation studies were done at 0 time (immediately after spiking the soils with pesticide) and after four-months incubation. Results show that soil properties greatly impact geochemical speciation and bioavailability of DMA; soils with high concentrations of amorphous Fe/Al oxides retain more arsenic, thereby rendering them less bioavailable. Results also indicate that the use of organic arsenicals as pesticides in mineral soils may not be a safe practice from the viewpoint of human health risk.

Keywords: Dimethylarsenic acid; Geochemical speciation; Bioavailability; Soil properties

1. Introduction

Arsenic is released into the environment in both inorganic and organic forms due to various natural as well as anthropogenic actions, and has been identified as a source of risk for human health even at relatively low concentrations (Hewitt et al., 1995). The United States Environmental Protection Agency (USEPA) has classified inorganic arsenic as a Group-A human carcinogen (Southworth, 1995). Weathering of arsenic-rich parent material and volcanic activity is the primary natural source of arsenic in soils (Van Herreweghe et al., 2003). The main anthropogenic sources of arsenic in soils include activities such as mining; smelting and fossil fuel combustion (Camm et al., 2004), wood preservatives (Chirenje et al., 2003), arsenic containing pesticides and herbicides (Gregory et al., 1996), pigments, growth promoters for poultry and pigs (Chirenje et al., 2003). The adverse effect of soil arsenic build-up on environmental quality and human health was realized relatively recently.

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In the late eighties and early nineties, the USEPA banned usage of many inorganic arsenic based pesticides (e.g., arsenic acid, lead arsenate, lead arsenite, copper arsenate, calcium arsenate etc.), but large areas of agricultural lands had already been contaminated. It is estimated that approximately 15 million pounds (equivalent to 6.8 million kilograms) of arsenic was applied to New Jersey soils between 1900 and 1980 (Murphy and Aucott, 1998).

Organic arsenicals such as monomethylarsenic acid (MMA) and dimethylarsenic acid (DMA) are considered to be less toxic (Pongratz, 1998), and are still allowed to be used as herbicides on agricultural lands, orchards, and golf courses. Little information is available on the fate and distribution of organic arsenicals in soils. The existing data indicates that there is a strong possibility of inter-conversion of organic and inorganic forms of arsenic in the soil system via chemical and biochemical oxidation-reduction reactions, with a net transformation to inorganic arsenic (Henry et al., 1979). This indicates that whether arsenic is applied in inorganic or organic form to the soil, it may ultimately transform into inorganic arsenic (Rodriguez, 1998). Hence, application of organo-arsenicals to agricultural lands may pose significant risks in future and the view that they are not potentially carcinogenic is inaccurate and requires immediate attention.

Ingestion of arsenic-contaminated soil due to incidental hand-to-mouth activity by children is being taken very seriously in assessing human health risks associated with arsenical pesticide-applied former agricultural soils, which are being converted to residential development in expanding metropolitan areas. A critical parameter that allows for more realistic health risk assessment in arsenic-containing soils is an estimate of bioavailable concentration of arsenic, rather than total soil arsenic (assuming 100% bioavailability) as recommended by the USEPA. Because calculated health risk is a direct function of the input value for chemical dose (Ng et al., 2003), the current USEPA-recommended practice of using an input value of 100% bioavailability for exposure to arsenic-enriched soils potentially overestimates the actual risk, thereby elevating the expenses associated with potential site-cleanup. The risk from arsenic exposure is associated only with those forms of arsenic that are potentially bioavailable in the human gastrointestinal system. It has been increasingly accepted that certain geochemical forms of arsenic are not bioavailable (Anawar et al., 2004). Although in vivo studies using animal models are the most appropriate methods for determining bioavailability of arsenic in soils, the time and costs prohibit their routine use. As a consequence, in vitro chemical methods (“beaker” models) simulating gastrointestinal conditions in the human gastrointestinal system have been developed in recent years.

Dimethylarsenic acid is the main organic metabolite of arsenic trioxide (As_2O_3), an inorganic arsenic derivative, and is considered to be a less toxic organic form of arsenic. Due to its common use as herbicide (Cai et al., 2002), DMA toxicology has been extensively studied (Kenyon and Hughes, 2001); however, the environmental fate, stability, distribution and bioavailability of DMA and other organo-arsenicals in soils are still incompletely understood. The main objective of the present study was to investigate the transformation, speciation and bioavailability of DMA as a function of soil properties. Two soils, similar in texture, but with vastly different arsenic retention capacities were selected for the reported study; both soils were spiked with DMA and incubated for a 4 months period. Comparative speciation and bioavailability studies were performed immediately after spiking the soils with pesticide and after the 4 months incubation period. The effect of soil properties on DMA transformation, speciation and bioavailability were investigated.

2. Materials and methods

2.1. Soil sampling, preparation and characterization

Two types of soils were used in this study—the Immokalee series and Millhopper series Spodosols. The Immokalee series soils were collected from surface horizons in the Southwest Florida Research and Education Center, Immokalee, Florida and the Millhopper series soils were collected from the surface horizons in the University of Florida campus at Gainesville, FL. The soils were selected to have varied amorphous Fe/Al oxide and organic matter contents to span a wide range of properties that are important for arsenic retention and/or bioavailability. Prior to their use, the soil samples were air-dried and passed through a 2 mm sieve. Selected soil properties, such as pH, electrical conductivity, particle size and water content were determined following standard methods of soil analysis (Klute, 1996). Soil organic matter content was determined using the loss-on-ignition method (Klute, 1996). Exchangeable cations were extracted by 1 M ammonium acetate (pH 7.0) and cation exchange capacity was determined by the removal of ammonium ions (Rhoades, 1982). Plant-available Ca, Mg and P were extracted by Mehlich III solution (Mehlich, 1984). Amorphous Fe/Al oxide concentrations were obtained using Tamm’s reagent method (Klute, 1996). Total P was extracted using the ignition method (Saunders and Williams, 1955). Total recoverable Ca, Mg, Fe, Al, P and As were determined by acid digestion according to the USEPA Method 3050B (USEPA, 1996).

The concentrations of P and Fe in the extracts and digests were determined colorimetrically using the molybdate–ascorbic acid method (Watanabe and Olsen, 1965) and 1,10-phenanthroline-reagent method (Olson

and Ellis, 1982), respectively, by a Varian Cary-50 UV–Visible light spectrometer. The concentrations of Ca, Mg and Al in the extracts/digests were analyzed using a Perkin–Elmer PE 700 atomic absorption spectrophotometer in the flame mode (FAAS). The digests were analyzed for arsenic using a graphite furnace attachment (GFAAS).

2.2. Soil amendments

Two hundred grams of each soil were spiked with DMA to achieve target concentrations of 45, 225, and 450 mg/kg (mass of arsenic/mass of dry soil), which represent background arsenic concentrations typically found at agricultural soils resulting from 1, 5 and 10 years of continuous pesticide application, respectively (Chisholm et al., 1955). Water content was maintained at 70% of the water holding capacity of the soils. The DMA was thoroughly mixed with soils, which were then stored in bags at room temperature. The soils were aerated weekly and constant water content was maintained. Arsenic was extracted from the soils immediately after pesticide amendment (within 2 h, since preliminary data (not presented) showed that DMA undergoes 100% adsorption onto the soils within 12 h) and after 4 months incubation period using a customized sequential extraction method and two in vitro procedures described below.

2.3. Sequential extraction procedure

Sequential extraction of arsenic was performed modifying the procedure reported by Chunguo and Zihui (1988) with a few modifications (Datta and Sarkar, 2004) for the following operationally-defined forms: (1) Water-soluble phase, (2) exchangeable phase, (3) Fe- and Al-bound phase, (4) Ca- and Mg-bound phase, (5) organic matter and sulfide-bound phase and (6) residual phase. The extracts were filtered and analyzed for As using the GFAAS.

2.4. In vitro extraction procedure

Bioavailable As was estimated following the in vitro gastrointestinal method of Rodriguez et al. (1999) with certain modifications developed by Sarkar and Datta (2003). All analyses were carried out in triplicate and results are shown as mean values.

3. Results and discussion

3.1. Soil properties

Chen et al. (1999) suggested that the retention and bioavailability of trace metals in soils are dependent on its pH, CEC, clay content, organic carbon content, and Fe and Al content. It is already reported that Fe and Al oxides phases of the soil form stable complexes with arsenic (Jacobs et al., 1970; Barringer et al., 1998) and therefore govern its retention and release from the soil. The physico-chemical properties of Immokalee and Millhopper series soils are shown in Table 1.

Table 1
Properties of soils

Properties	Immokalee	Millhopper
pH	6.0	6.4
EC[a] (μS/cm)	59	145
CEC[b] (Cmol/kg)	777	2356
SOM[c] (%)	0.84	4.38
As (mg/kg)	15.0	16.5
P (mg/kg)		
Mehlich 3	4.0	134
Total	208	4875
Ca + Mg (mg/kg)		
Mehlich 3	266	886
Total	1178	3155
Fe + Al (mg/kg)		
Oxalate	66	704
Total	212	4745

[a] EC = electrical conductivity.
[b] CEC = cation exchange capacity.
[c] SOM = soil organic matter.

There was no significant difference in the pH of Immokalee and Millhopper soils; both are acidic with pH values of 6.0 and 6.4, respectively. Millhopper soil has relatively high organic matter content, salinity (measured as EC), and cation exchange capacity compared to the Immokalee soil. Further, low total and extractable Fe/Al, Ca/Mg, and P contents characterize the Immokalee soil, while Millhopper soil has high total and extractable Fe/Al, Ca/Mg, and P contents. Hence, it may be presumed that the high amorphous Fe/Al content of the Millhopper soil will increase the soil surface area as well as the density of positively charged sites, which in turn will potentially reduce the bioavailablity of the oxyanions of arsenic. On the other hand, the Immokalee soil with less Fe and Al content is likely to have minimal arsenic retention capacity (Pierce and Moore, 1980; Oscarson et al., 1981), thereby potentially increasing the bioavailable fraction of arsenic. This study uses Immokalee soil essentially as a control to verify the effects of high concentrations of Fe, Al, and P in addition to organic and clay content present in Millhopper soil on arsenic bioavailability.

3.2. Geochemical forms of arsenic

Chemical speciation of As in soil is the process of identification and quantification of the various species, forms or phases occurring in the soil. Analysis of such geochemical forms is important because it can provide

crucial information on reactivity, bioavailability and toxicity of As. Sequential extraction is a process by which the soil sample is reacted with a series of solutions to selectively extract distinct geochemical fractions (Pickering, 1981). Consequently, a six-step sequential extraction scheme was developed to characterize the geochemical behavior and mineralogical forms of arsenic by subsequently reacting soil sample with predetermined extractants. In general, water-soluble (step 1) and exchangeable (step 2) forms are considered to be weakly bound and may equilibrate with the aqueous phase thus becoming readily bioavailable. On the other hand, the arsenic in residual fraction (step 6) is not released under normal conditions. The other forms like Fe/Al bound (step 3), complexes of Ca/Mg (step 4), and organic matter (step 5) provide a sink or reservoir for arsenic and considerably influence its bioavailability. In contrast, phosphorous content of the soil may contribute to the dissolution and release of arsenic from the soil matrix.

The distribution of DMA in different chemical phases within Immokalee and Millhopper soils was investigated at two time frames (0 time and 4 months) at 45 mg/kg of arsenic loading rate (Fig. 1). The fractionation of arsenic in Immokalee soil shows that nearly 88% of arsenic was leached out as water soluble fraction and 8% of arsenic was extracted in an exchangeable form, immediately after spiking the soil with DMA pesticides (0 time). Only 3% of arsenic was associated with Fe/Al oxide fraction, while other forms including the organic phase constituted less than 1% of the total arsenic amended. After

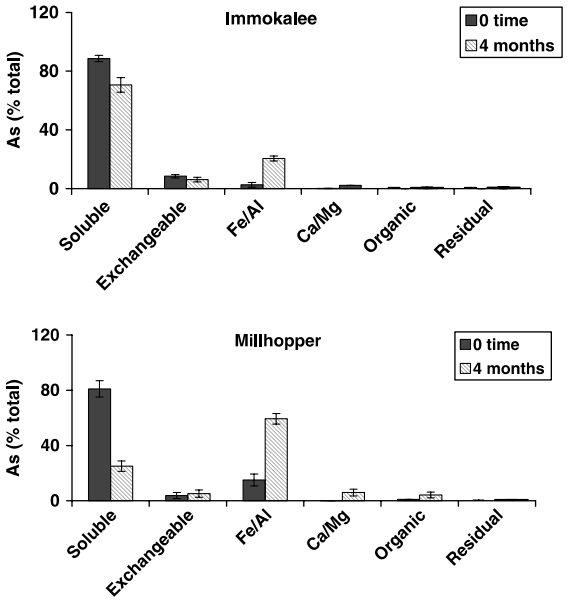

Fig. 1. Geochemical speciation of arsenic in pesticide applied soils (45 mg/kg As) at time zero and after 4 months equilibration.

4 months incubation period, the amount of arsenic extracted in the soluble fraction decreased from 88% to 70% with an increase in Fe/Al bound fraction from 3% to 20%. Negligible arsenic (0.15%) was found associated with organic matter. The data obtained indicate that at 0 time organo-arsenicals may leach from sandy soils because they bind to the soil matrices less strongly. These results are in agreement with the data reported by Woolson and Kearney (1973). In such cases, where the binding is poor, there is a possibility that the DMA may not be resident long enough to change its speciation under leaching conditions encountered in field scenarios. Based on the results obtained from static incubation studies, such possibility cannot be neither confirmed nor disproved; a greenhouse column study that allows for dynamic interactions between pesticides, soils, water, and plants is currently in progress to resolve such questions.

In the Millhopper soil, the amount of arsenic extracted in the soluble fraction (81%) was similar to that in Immokalee at 0 time indicating lack of soil pesticide equilibration. Interestingly, 15% of arsenic was extracted from the Fe/Al bound fraction at 0 time, while approximately 1% of arsenic was retained by organic phase. This indicates that the high amorphous Fe/Al content is capable of retaining significant amount of arsenic immediately after the soil amendment. Other fractions showed negligible retention of arsenic. After 4 months incubation period, soluble fraction of arsenic decreased significantly to 25%, and the retention of arsenic by Fe/Al fraction increased 4-fold (15–60%). Decrease in arsenic concentration in the soluble fraction coupled with the corresponding increase in the Fe/Al bound fraction indicates the effect of equilibration time/ageing on arsenic speciation.

No noticeable change in the exchangeable arsenic fraction was observed in Millhopper soil after 4 months, whereas slight increases of arsenic in the Ca/Mg bound phase (6.0%) and organic fraction (4.5%) was observed. These results indicate that DMA was potentially transforming into more stable inorganic arsenic in soil systems and the degree of transformation was a function of soil type and interaction time. Woolson (1983, 1989) suggested that two types of oxidation are generally responsible for the transformation of organo-arsenicals to inorganic arsenic oxyanions: in one type, the carbon–arsenic bond is destroyed primarily due to microbial activity and in the other type, the change in oxidation state of arsenic is due to the interaction with soil mineral phases. In these experiments, either or both of these oxidation mechanisms may have played a role in transforming organo-arsenical species into more stable inorganic arsenic oxyanions, which were then strongly adsorbed by the hydrous Fe/Al phases in the Millhopper soil. Sorption is probably the most important fate-controlling mechanism determining the transformation and soil speciation of arsenic. Previous studies have

demonstrated that at low to moderate pH, arsenic undergoes irreversible specific adsorption onto Fe/Al oxyhydroxide (Bowell, 1994; Goldberg and Johnston, 2001; Arienzo et al., 2002). Further, arsenic adsorbed irreversibly to Fe/Al oxides is considered to be unavailable for plant uptake, and is also relatively unavailable in the human gastrointestinal systems (Rodriguez, 1998).

Similar results were obtained for soils contaminated with 225 and 450 mg/kg of arsenic in the form of DMA (data not shown). These findings suggest that DMA has the potential to become significantly mobile in sandy soils, particularly those with low amorphous Fe/Al oxide contents. Even in soils with high Fe/Al, arsenic from DMA may become available for leaching through the soil profile immediately after pesticide application. With increasing equilibration time, DMA is potentially transformed to inorganic arsenic oxyanions, which are effectively retained in soils with high sorption capacity.

3.3. Estimation of bioavailable arsenic

Ruby et al. (1993) developed the "physiologically based extraction test" (PBET) to predict in vitro metal bioavailability. Two important mechanisms are involved in digestion of arsenic contaminated soil: solubility of the contaminant in the digestive juices, and absorption of metal across the intestinal membrane (Rodriguez et al., 1999). While most of the studies so far have estimated the amount of metals solubilized under gastrointestinal conditions, only two reported studies have taken the intestinal absorption of metals into account while estimating soil–arsenic bioavailability (Rodriguez et al., 1999; Sarkar and Datta, 2003). In the current study, the method developed by Sarkar and Datta (2003) was followed to estimate arsenic bioavailability in the intestinal system.

Data obtained from the in vitro gastrointestinal bioavailability studies are presented in Fig. 2. The gastric phase (IVG-stomach) extracted 100% of amended arsenic at 0 time from both soils studied. However, after the 4 months incubation period, the percentage of arsenic extracted by IVG-stomach phase significantly decreased to 80–53%, respectively, in the Immokalee and the Millhopper soil. The intestinal phase (IVG-adsorbed-intestinal) extracted higher amounts of arsenic than the stomach phase from both soils incubated for 4 months. At 0 time, 100% of spiked arsenic was bioavailable, which decreased to 88% in Immokalee and to 72% in Millhopper soil after 4 months equilibration.

Similar trends were observed in soils contaminated with 225 and 450 mg/kg of arsenic in the form of DMA (data not shown). Decreased bioavailability of arsenic in both soils after 4 months (relative to the widely practiced water model that assumes 100% bioavailability) depended upon the extent of transformation of DMA to inorganic soil arsenic species with lower solubility. Arsenic was more strongly retained by the abundant Fe/Al oxyhydroxides in the Millhopper soil, and was relatively more stable (hence, less bioavailable) compared to the Immokalee soil.

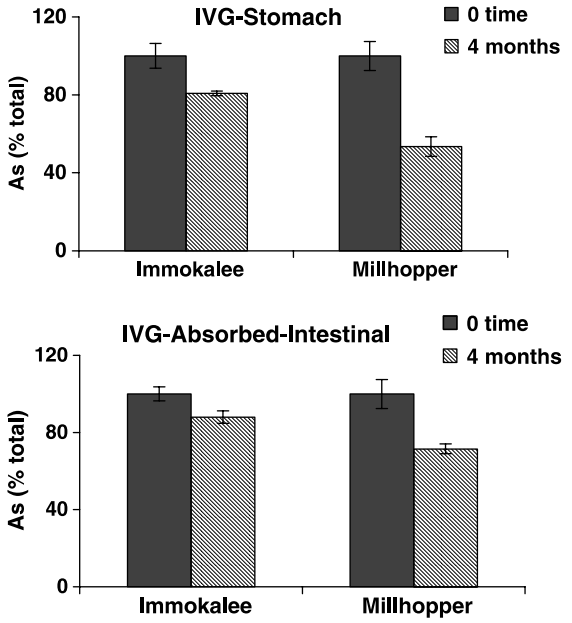

Fig. 2. Arsenic bioavailability in pesticide applied soils (45 mg/kg As) using two different in vitro methods at time zero and after 4 months equilibration.

3.4. Correlation between geochemical speciation and bioavailability

Correlation between arsenic extracted by in vitro gastrointestinal–stomach method with arsenic extracted by different steps of sequential extraction scheme for the Immokalee and Millhopper soils amended with 45, 225, and 450 mg/kg arsenic at two time frames (0 time and after 4 months incubation) are shown in Fig. 3a and b, respectively. Bioavailable arsenic was significantly correlated (correlation coefficient varied between 0.66 and 0.85) with the soluble fractions at 0 time (immediately after spiking) as well as after the 4 months incubation period in Immokalee (Fig. 3a). Bioavailable arsenic did not correlate significantly with other geochemical phases of Immokalee soil at 0 time. However, after the 4 months incubation period, correlation between bioavailable and Fe/Al-bound fractions of arsenic increased from 0.54 to 0.78 in the Immokalee soil system (Fig. 3a).

On the other hand, although bioavailable arsenic exhibited high correlation with soluble arsenic at 0 time

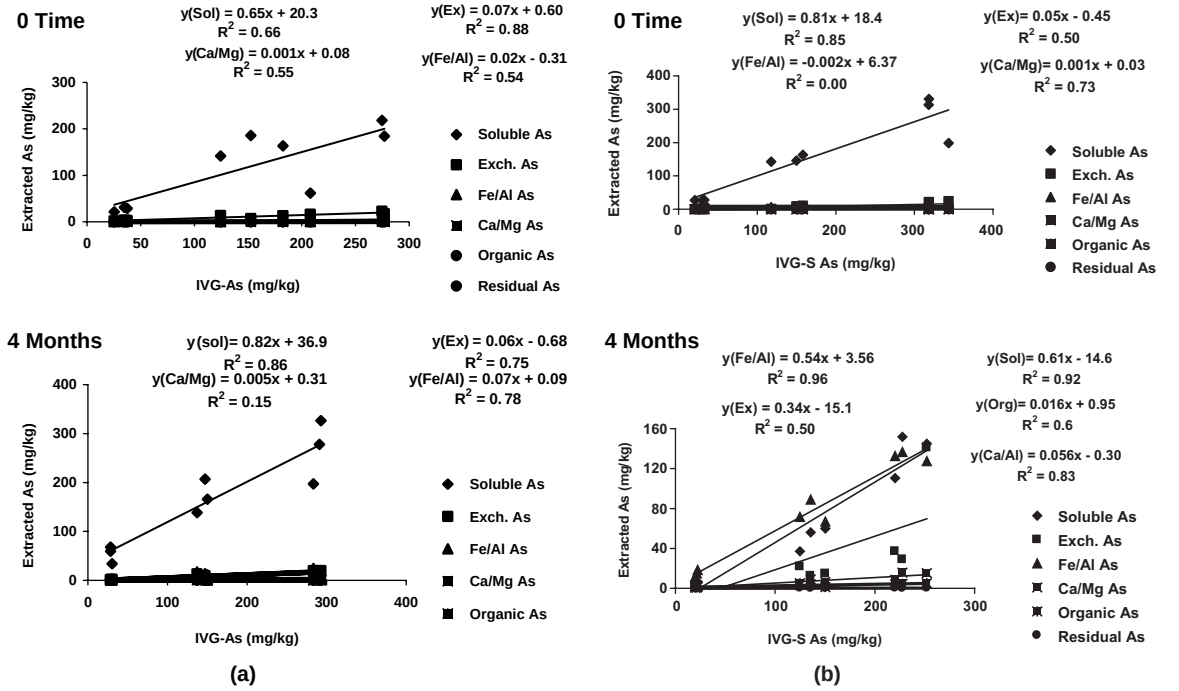

Fig. 3. Relationship between bioavailable arsenic estimated using the IVG-S method and arsenic geochemical forms at time zero and after 4 months equilibration in: (a) Immokalee and (b) Millhopper ($n = 3$).

(0.85) and after 4 months equilibration (0.92) in the Millhopper soil, the correlation between Fe/Al bound arsenic and bioavailable arsenic increased significantly (from 0.0 to 0.96) as the equilibration time increased from 0 time to 4 months (Fig. 3b). This indicates that the equilibration time of 4 months may be insufficient for complete transformation of DMA to inorganic Fe/Al-bound arsenic species in this soil. A metastable As-Fe/Al phase may have formed which underwent further re-dissolution when exposed to the strongly acidic and reduced conditions of the simulated gastric juice. Other soil arsenic phases, such as Ca/Mg-bound and organically-complexed arsenicals also showed a noticeable increase in their correlation with bioavailable arsenic, as evident from the increase in slope values of the regression lines. These results indicate that DMA, which is considered to be a non-carcinogenic, relatively less toxic organo-arsenical species, may undergo chemical transformation to the more toxic and carcinogenic inorganic arsenicals when exposed to a strongly reducing environment, such as the human gastrointestinal system, thereby questioning the validity of the current USEPA policy that still allows usage of organic arsenic as pesticides in soils. Similar results were obtained when sequentially-extracted arsenic was correlated with bioavailable arsenic obtained by the IVG absorbed-intestinal method (data not shown).

3.5. Correlation between IVG-S and IVG-AI methods

Data obtained from two IVG methods were correlated for the Millhopper and Immokalee soils contaminated with 45, 225, and 450 mg/kg of arsenic (Fig. 4). A correlation coefficient of 0.95 was obtained, indicating that results from both methods were statistically similar, and that both in vitro methods were extracting arsenic from similar soil arsenic pools in the soils.

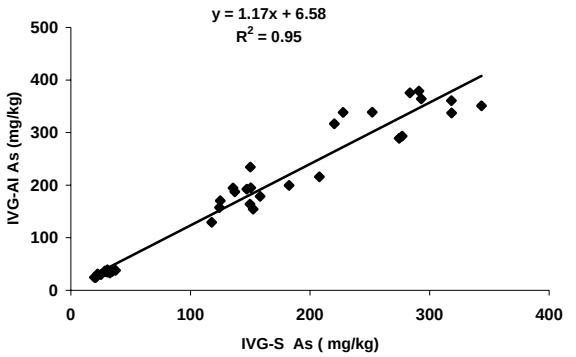

Fig. 4. Correlation between arsenic extracted by the two in vitro methods. Data has been pooled for Millhopper and Immokalee soils contaminated with 45, 225, and 450 mg/kg As ($n = 3$).

4. Conclusions

This study demonstrated that soil properties have a marked impact on geochemical speciation of arsenic. Using two soils with differing chemical properties, we showed that soil chemistry dictates geochemical speciation of arsenic, and that arsenic bioavailability is mostly a function of its geochemical speciation. In the Millhopper series soil, which has high amounts of extractable Fe/Al, arsenic bioavailability decreased markedly after 4 months incubation, compared to the Immokalee series soil, with low Fe/Al content. Bioavailable arsenic exhibited high correlation with soluble and exchangeable arsenic in both Immokalee and Millhopper. In Millhopper, correlation between Fe/Al bound arsenic and bioavailable arsenic increased significantly with equilibration time. Other soil arsenic phases, such as Ca/Mg-bound and organically-complexed arsenicals also showed a noticeable increase in their correlation with bioavailable arsenic with increasing equilibration time. Results indicate that DMA, which is considered to be a relatively less toxic organo-arsenical species, undergoes chemical transformation to potentially carcinogenic inorganic arsenicals when exposed to a strongly reducing environment of the human gastrointestinal system, thereby questioning the validity of the current USEPA policy that still allows the use of organic arsenic as pesticides.

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